Fluorescence and excitation spectra of Ag_4 in an argon matrix

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Abstract

We report the fluorescence and excitation spectra of size selected Ag_4 deposited in an argon matrix. The main fluorescence peak for Ag_4 is observed at 458 nm. The excitation spectrum for this emission is in good agreement with recent theoretical calculations and photodepletion experiments.

Optical spectroscopy is a powerful technique to study the electronic structure of small clusters. However, direct optical absorption measurements of free mass selected clusters is at least at present not possible since sufficiently large cluster densities are not available. Small silver clusters have been investigated in free beam experiments, using techniques like resonant two-photon ionization spectroscopy [1,2], laser-induced fluorescence [3], pump-probe [4,5] or photodepletion [6,7] techniques. Alternatively matrix isolation experiments [8], where fragmentation has proven to be low [9], have provided absorption spectra for cluster sizes up to $n = 39$ [10]. Fluorescence spectra however are only reported for the atom, dimer and trimer [8]. For larger metal clusters, rapid radiationless processes compete effectively with the radiative processes [11–13] and therefore it was commonly assumed that there was no fluorescence for $n > 3$. In this paper, we report the first observation of the fluorescence of the silver tetramer in an argon matrix as well as the corresponding excitation spectrum. The excitation spectrum is compared to recent *ab initio* calculations as well as to recent photodepletion measurements and found to be in good agreement with both of them.

The production and mass selection of the positively charged silver cluster

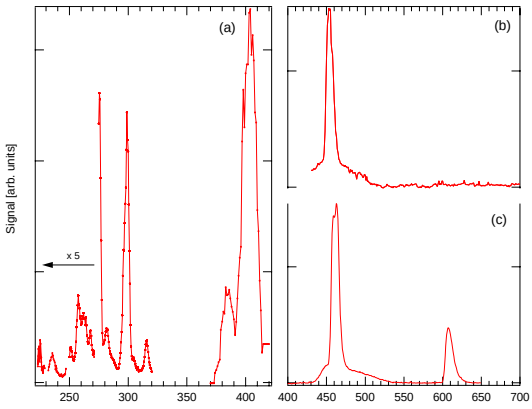

Fig. 1. Fluorescence and excitation spectra of Ag_4 in Argon matrix. a) Excitation spectrum measured at 458 nm b) Fluorescence spectrum excited at 405 nm c) Fluorescence spectrum excited at 387 nm

has been described in detail elsewhere [14]. The experimental setup has been modified by the addition of a pumping stage and a perpendicular deflection of the cluster beam. This allows to reduce contamination from the source and for better control of the matrix growth. Briefly, silver ions are sputtered from a silver target using an intense and high energy xenon-ion beam (typically 10 mA, 24 keV). They are extracted by a lens system and mass selected by a commercial quadrupole mass filter. The mass selected cluster ions are deflected by 90^0 with a quadrupole. This acts as a filter for the neutral silver particles as well as an energy filter for the cluster ions. The pressure of argon in this deflection chamber is about 10^{-4} mbar and a neutral argon beam is formed toward the deposition chamber. The positively charged clusters are focused by a second lens system on a cold (< 25 K) sapphire plate, where they are co-deposited with the Ar to form a matrix. Neutralization of the cluster ions is achieved by an electron cloud maintained close to the deposition window. Fragmentation of the incoming cluster beam takes place, but the percentage of the fragments is low as discussed in detail in [9]. The deposition energy of the silver clusters is $E_{Dep} = 30$ eV with a typical current for the Ag_4^+ of 1 nA. Clusters are deposited for about two hours on a spot of 2 by 3 mm, leading to a surface density of $\sim 10^{15}$ cm^{-2} with an Ar:cluster ratio of $\sim 10^4 : 1$.

Matrix samples are studied *in situ* using excitation and fluorescence spectroscopy. For the excitation we use a frequency doubled Optical Parametric Oscillator (OPO) pumped by a Nd:YAG Laser. Accessible wavelengths in UV region range from 220 to 340 nm and from 370 to 440 nm. The fluorescence is collected, collinearly to the outgoing laser beam, by a lens to form a parallel beam. The collected parallel beam is then focalized in the entrance slit of a spectrometer coupled to either a liquid nitrogen cooled Charge Coupled Device (CCD) detector or a single-channel photomultiplier (PM) detection system. The signal is corrected for laser pulse intensity.

Figure 1.b) shows the fluorescence spectrum of Ag_4 for an excitation of $\lambda =$ 405 nm (measured with a PM detection system with a matrix temperature maintained at 25 K). For this excitation wavelength we observe a fluorescence peak at 458 nm. No other peak can be seen in the rest of the spectrum. This fluorescence is new and cannot be assigned to fluorescence peaks of Ag_1, Ag_2 and Ag_3 [8] which could possibly result from a fragmentation process during the deposition. The fluorescence spectrum when exciting with 387 nm (recorded with a CCD camera and the temperature of the matrix maintained at 15 K) shows two fluorescence peaks (Fig. 1.(c)), one double peak at 458/463 nm [15] and a second one at 608 nm. The peak at 608 nm can be assigned to the silver trimer, this is an indication for fragmentation of the impinging tetramer in trimer and monomers. The silver dimer has an emission band centered around 479 nm which is not observed, we conclude therefore that the fragmentation channel for the production of silver dimers is weak. Fluorescence of the silver monomer has a peak at 458 nm [8] but it is about five times broader than the one we observe and therefore we can confidently assign the observed fluorescence to the tetramer. Additionally we have checked that the shape of the fluorescence peak does not change with the excitation wavelength, which prooves that it is due to a unique species.

The excitation spectrum (Fig.1.(a)) recorded by changing the excitation wavelength while recording the fluorescence intensity at 458 nm shows several peaks, a first one at 405 nm and a less important one at 387 nm, where the fluorescence spectra ((Fig.1.(b) and (c)) were recorded. Two other important peaks are found at 299 and 273 nm.

All these peaks are attributed to Ag_4. A weak monomer signal is observed since Ag_1 fluorescence is centered at $\lambda = 458$ nm (see above). Ag_1 is produced via the fragementation channel $Ag_4 \longrightarrow Ag_3 + Ag_1$. The absorption at 314.5 nm can be assigned to the silver atom and there should be additional peaks at 304 and 298 nm [8]. The 304 nm peak is in the shoulder of the neighboring absorption band of Ag_4, while the 298 nm peak is hidden by it. As the three atomic absorption lines have about the same magnitude, contribution from the atom to the peak at 299 nm is small. It can therefore be assigned mainly to Ag_4. This is confirmed by the fluorescence spectrum (not shown) recorded at 299 nm excitation, which has the same shape as in Fig. 1.(b) with a peakwidth of around 20 nm. The shape of the $\lambda = 273$ nm excitation peak could not be measured completely because of insufficient laser light intensity around 272 nm; however it seems much sharper than usual absorption peaks. It is reproducible and the corresponding fluorescence peak is identical in shape and position to the one showed in Fig. 1.(b). Because of incompleteness of information we will not discuss this peak further. There are some additional bands between 250 and 270 nm with low intensity compared to the absorption bands already discussed above. The fluorescence spectra of these peaks have again the same shape. With this indication we can also assign them to the

Table 1
Absorption bands and principal corresponding emission for the silver tetramer. Values in brackets refer to additional fluorescence bands with lower intensities not discussed in this paper. Units are in nm.

Specie	Absorption band	Principal corresponding fluorescence band
Ag_4	405	458
	386	458
	299	458
	295	(481)
	275	(519)
	273	458
	268	458
	262	458
	258	458
	251	458
	235	458

silver tetramer.

The detected absorption bands together with their principal corresponding emission bands are summarized in Table 1.

Recently theoretical calculation of the transition bands and their corresponding oscillator strength for silver dimer, trimer and tetramer have been performed by V. Bonaĉić-Koutecký *et al.* [16]. The two most stable isomers of Ag_4 have D_{2h} and C_{2v} symmetries. The oscillator strength for these two structures are compared to our results in the Figure 2(c) and 2(d). The behavior in the low energy region (< 4.7 eV) is similar for the two isomers, only the position and distance between the two peaks vary slightly. Remarkable differences between the two geometrical structures only appear in the high energy region.

The theoretical spectra are compared to our results (Fig. 2(a))and to the absorption spectrum of Ag_4Kr_2 in gas phase (Fig. 2(b)) measured by Hacket et al. [7] using a photodepletion technique. The agreement between the two experimental results is good although we measure additional peaks at 3.2 and 4.5 eV (see below). Notice however that the 4.15 eV (299 nm) absorption in the matrix is blue shifted by 0.1 eV.

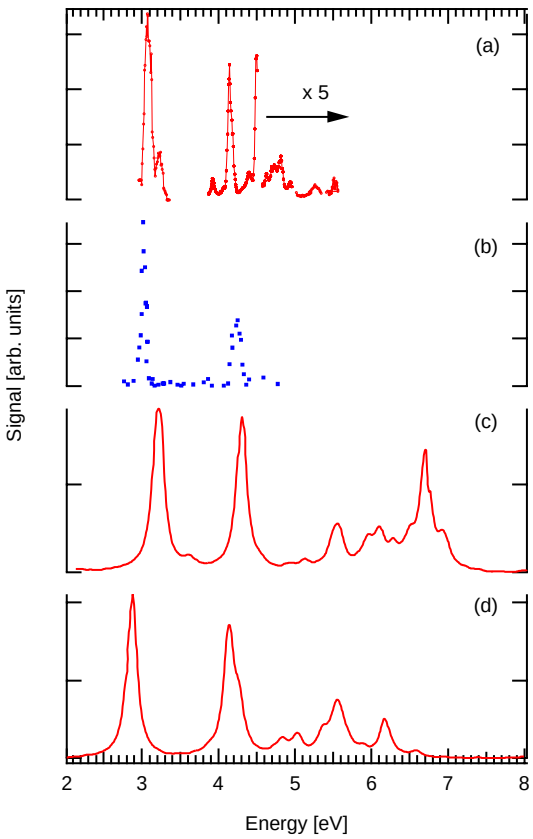

Fig. 2. Absorption Spectrum a) Our results b) Photodepletion spectrum of Ag_4Kr_2 *(after Hackett and coworkers [7])* c) Calculated transitions for the D_{2h} structure *(after [16])* d) Calculated transitions for the C_{2v} structure *(after [16].)*

For a detailed comparison of the experiments with the calculated spectra, we would have to account for the matrix effects, which are difficult to predict for small particles. A difference of more than 0.1 eV between the calulated peak at 3.1 eV and the two calculated spectra is observed. The local maximum at 3.2 eV coincides with the maximum of the D_{2h} structure. Between 4 and 5 eV, we observe two major peaks at 4.15 and 4.5 eV whereas the calculated spectra only have one transition for each geometrical structure. The first absorption lies at the same position as the position calculated for the C_{2v} structure, whereas the second absorption is 0.2 eV beside the D_{2h} absorption. As the two calculated spectra are too similar in the accessible energy range for our measurements, it is not possible to decide for one or the other geometry based on our data. In fact, we may well have a mixture of both structures in the matrix. It would however be surprising that they have the same fluorescence signature.

As a conclusion, the fluorescence of Ag_4 embedded in an argon matrix is observed for the first time. The major fluorescence peak is situated at 458 nm with a bandwidth of only 20 nm. The excitation spectrum recorded for this fluorescence is in good agreement with recent theoretical calculations as well

as with recent photodepletion experiments. The calculated absorption spectra of the two configurations of the tetramer are too similar in the observed energy region to decide, based on our measurements, which of two most stable geometrical structures we observe.

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